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TITLE: Heat reservoir structure for incorporating in building materials - comprises small pellets of encapsulated phase-change compsn.

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GB 2142135 A	January 9, 1985	N/A	000	N/A
US 4504402 A	March 12, 1985	N/A	000	N/A
US 4505953 A	March 19, 1985	N/A	000	N/A
US 4513053 A	April 23, 1985	N/A	000	N/A
CA 1207139 A	July 8, 1986	N/A	000	N/A
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GB 2142135 B	June 24, 1987	N/A	000	N/A
IT 1170460 B	June 3, 1987	N/A	000	N/A
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DE 3338009A	N/A	1983DE-3338009	October 19, 1983
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JP 60004792A	N/A	1983JP-0162707	September 6, 1983
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ABSTRACTED-PUB-NO: DE 3338009A

BASIC-ABSTRACT:

Layer or composite prod. (I) contains (a) outer shell part of max. dimension approx. 0.31-2.54 cm., with inner surfaces forming on internal cavity suitable for permanently enclosing a phase-change storage compsn. (II) for thermal energy, shell consisting of at least one seamless or jointless layer of a wall-forming material substantially impermeable to, and not reactive with (II) or water and total vol. of wall-forming material being about 5-30% vol. of cavity; (b) a (II) permanently arranged inside the cavity, suitable for occurrence as solid, molten liq., or intermediate forms, and in amt. such that its total vol. in any of these forms does not exceed vol. of cavity.

ADVANTAGE - (I) is suitable for incorporating into stiff building materials

(e.g. concretes, including polymer concretes, also plaster) without breakage or damage to materials or (I) after repeated thermal treatment of (I). Prod. size is intermediate between large plastic spheres and microcapsules previously proposed for heat storage, being small enough to permit sufficient heat transfer and prevent possible phase sepn. but large enough for mass prodn. at low cost.

ABSTRACTED-PUB-NO: DE 3338009C

EQUIVALENT-ABSTRACTS:

Layer or composite prod. (I) contains (a) outer shell part of max. dimension approx. 0.31-2.54 cm., with inner surfaces forming an internal cavity suitable for permanently enclosing a phase-change storage compsn. (II) for thermal energy, shell consisting of at least one seamless or jointless layer of a wall-forming material substantially impermeable to, and not reactive with (II) or water and total vol. of wall-forming material being about 5-30% vol. of cavity; (b) a (II) permanently arranged inside the cavity, suitable for occurrence as solid, molten liq., or intermediate forms, and in amt. such that its total vol. in any of these forms does not exceed vol. of cavity.

ADVANTAGE - (I) is suitable for incorporating into stiff building materials (e.g. concretes, including polymer concretes, also plaster) without breakage or damage to materials or (I) after repeated thermal treatment of (I). Prod. size is intermediate between large plastic spheres and microcapsules previously proposed for heat storage, being small enough to permit sufficient heat transfer and prevent possible phase sepn. but large enough for mass prodn. at low cost.

GB 2142135A

A method for the manufacture of a thermal energy storage capsule, which comprises forming discrete quantities of a thermal energy storage material into coherent solid bodies having an apparent density that is equal to or less than the liquid phase density of said material, said material being capable of undergoing a reversible phase change from solid to liquid, or to an intermediate transitional state comprising both solid and liquid, over a given temperature range, coating said solid bodies with one or more continuous layers of a heat curable, liquid wall-forming material that is stable over said temperature range and capable, when cured, of forming a self-supporting seamless capsule wall completely surrounding each respective body of thermal energy storage material, the thickness of the applied layer or layers of wall-forming material being such that the total volume occupied by the material forming the finished capsule wall is from 5 to 30% of the volume inside the capsule, heating the coated bodies to a temperature not above the melting point of the thermal energy storage material thereby to cure said layer or layers of wall-forming material and thereby to form a thermal energy storage capsule comprising said liquefiable thermal energy storage material encapsulated within a completely self supporting seamless capsule.

GB 2142135B

A method for the manufacture of a thermal energy storage capsule, which comprises forming discrete quantities of a thermal energy storage material into coherent solid bodies having an apparent density that is equal to or less than the liquid phase density of said material, said material being capable of undergoing a reversible phase change from solid to liquid, or to an intermediate transitional state comprising both solid and liquid, over a given temperature range, coating said solid bodies with one or more continuous layers of a heat curable, liquid wall-forming material that is stable over said temperature range and capable, when cured, of forming a self-supporting seamless capsule wall completely surrounding each respective body of thermal energy storage material, the thickness of the applied layer or layers of wall-forming material being such that the total volume occupied by the material forming the finished capsule wall is from 5 to 30% of the volume inside the capsule, heating the coated bodies to a temperature not above the melting point

of the thermal energy storage material thereby to cure said layer or layers of wall-forming material and thereby to form a thermal energy storage capsule comprising said liquefiable thermal energy storage material encapsulated within a completely self supporting seamless capsule.

US 4504402A

Thermal energy storage composite prod. (I) comprises (a) an outer shell member having a longest dimension of 1/8 to 1 inch and having interior surfaces defining only a single internal cavity which is adapted to permanently encase a thermal energy storage phase-change compsn., the shell

comprising at least one seamless layer of a wall-forming material which is impermeable to, and non-reactive with the phase-change compsn. or water, the total vol. of the wall-forming material being 5-30% of the vol. of the cavity.

(b) a thermal energy storage phase-change compsn. permanently disposed within the single cavity of the shell, the phase-change compsn. being capable of existing in solid form, a melted liq. form or a transition state which includes both the liq. and the solid forms, the compsn. being present in an amt. such that the total vol. of the compsn. whether in solid- or liq-form, or in the transition state, does not exceed the vol. of the cavity.

USE - (I) can be incorporated within rigid

building construction components without causing fracture or damage to the components or prod. after the prod. undergoes repeated thermal change cycles.

(10pp)

US 4505953A

Thermal energy storage phase-change composite prod. (I) is produced by a) selecting a thermal energy storage phase-change compsn. having a phase-change transition temp. within the temp. range of the contemplated environment in which (I) is to be used, and holding the temp. of the compsn. below the m.pt. of the compsn., after the compsn. has been first melted, to provide a solidification thermal energy phase-change compsn.

b) converting the compsn. produced in a) to a flowable powder compsn. while holding the compsn. below its m.pt.

c) compacting and pelletising the powder compsn. from b) to form discrete pellet-shaped compacted powder structures (II) having a longest dimension of

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GB A 2084311 WO 8001073
GB 1011104 WO 8000257
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(58) Field of search
F4U

(54) Thermal energy storage capsules for use in structural building elements

(57) A thermal energy storage capsule comprises a thermal energy storage material 17 capable of undergoing a reversible solid-to-liquid phase change, encapsulated in a multilayer capsule 18 to 23 having a maximum external dimension in the range 3.2 to 25.4 mm and defining a cavity containing the phase change material, the amount of which is such that the volume of the phase change material, i.e. liquid or solid, is equal to or less than the volume of the cavity. The capsules are used as thermal energy storage members in structural building elements of concrete or gypsum.

The capsules are made by forming compacted or agglomerated cores of the phase change material having an apparent density less than that of the corresponding molten liquid, casting the capsule around the core, melting the core, and allowing the melt to resolidify inside the capsule.

Preferred thermal storage materials and capsule wall materials are disclosed.

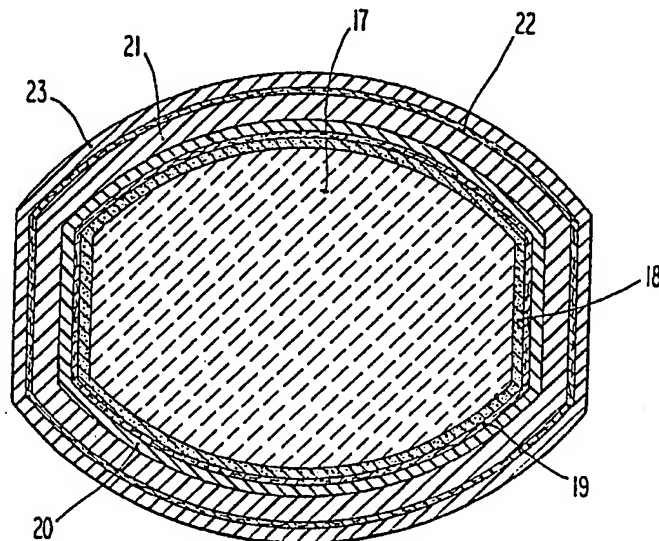


Fig. 2

GB 2 142 135 A

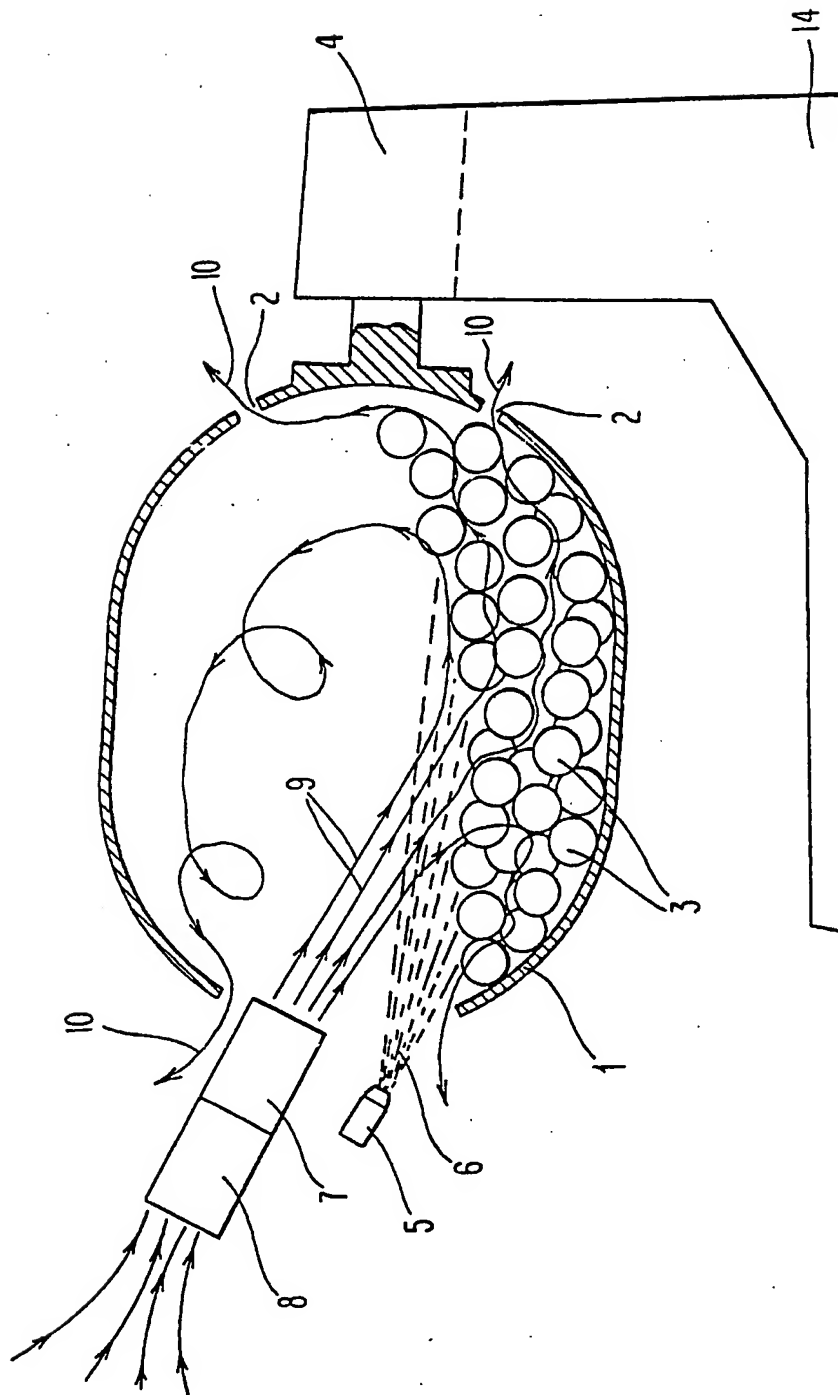


Fig. 1

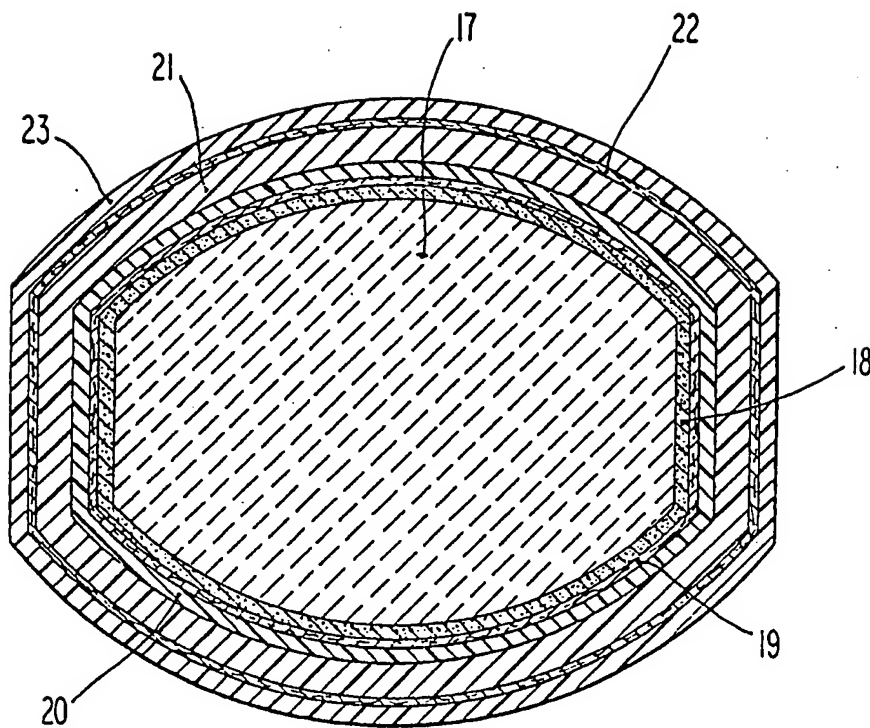


Fig. 2

SPECIFICATION

Thermal energy storage capsules process for the manufacture thereof and structural building elements containing them

Thermal energy storage technology is important because it saves energy, provides economic benefits, and permits the convenient use of periodic energy sources, such as solar energy. Certain thermal energy storage systems using the specific heat of water, rocks, and ceramics are already commercially available. Systems that contain phase change materials are being developed because a high energy storage density is associated with the change of phase. Long term thermal energy storage can be achieved by means of heats of solution, hydration, and reaction of certain chemicals. All of these thermal energy storage materials have one or more of the following technical difficulties that must be overcome: agglomeration, component separation, supercooling, large volume in comparison with thermal capacity, low thermal conductivity, expensive heat exchanger requirements, corrosion of container walls, incompatibility with system components, and limited surface area.

One attempted method to circumvent these problems was to form construction composites of the thermal energy storage materials with concrete or plastics, but new problems of seepage, component incompatibility, and reduced thermal conductivity occurred. Brookhaven National Laboratory reports BNL 50827 (August 1977 - February 1978) and BNL 50896 (March 1978 - May 1978), for example, discuss the problems with, and failures experienced in, attempting to incorporate phase change materials, both the inorganic salt hydrate (e.g., $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \cdot \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and organic (e.g. fatty acids, polyethylene glycol) types, into ordinary concrete, polymer-impregnated concrete and polymer concrete. The project met with limited success in its attempts to introduce phase change materials into concrete, and that little success was primarily achieved using foamed glass beads impregnated with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The incorporation of thermal energy storage materials into plastics is disclosed in U.S. Patent No. 4 003 426. The thermal energy storage material is dispersed into an uncured polymeric resinous matrix which is then cross-linked. As stated in the patent, this method is useful only with thermal energy storage materials which will form stable dispersions in the uncured polymer and requires the envelopment of the cured structure in a gas or vapor barrier material for best results.

Another attempted method for overcoming the problems was macro-encapsulation. In this case, thermal energy storage materials about 1 inch (25 mm) diameter or larger are jacketed with multilayer flexible plastics/metal film composites, steel cans, or polyolefin bottles. This approach may be useful for certain applications but commercialization has been hampered by poor thermal conductivity, deformation of the packages, and degradation of the encapsulating materials by chemical attack and mechanical stresses.

Still another approach is microencapsulation. Research on thermal energy storage systems containing microencapsulated wax demonstrated the need for encapsulated thermal energy storage materials and the technical feasibility of their use. The results provided that microencapsulated thermal energy storage material can be packed into a bed through which heat exchange fluid passes. In this manner the heat exchange fluid directly contacts the heat storing material. The results also included improved thermal conductivity, reduced complexity in the heat exchanger, reduced thermal energy storage material separation problems, and reduced equipment cost. However, overall system costs were found to be too high with first generation microencapsulated thermal energy storage material due to the high processing costs of the encapsulating procedure. This work is described in report NSF/RANN/SE/AER 74-09186, dated November 1975. Subsequent work has not significantly altered these conclusions.

One of the principal goals of microencapsulation was to reduce thermal conductivity path lengths in heat transfer systems by reducing the size of the discrete thermal energy storage material particles employed. Capsules were made by coating paraffin particles in the 8-2000 micron (0.003" - 0.08") range with wall-forming materials, such as gelatin (which was generally unsatisfactory), modified nylon and urea-formaldehyde resin. It was observed that the 50 micron nylon-coated particles exhibited no leakage after 300 thermal cycles, while the 1000-2000 micron samples exhibited some leakage after 150 cycles. These results notwithstanding, the optimum cost that could be achieved using the microencapsulation techniques of the prior art was three to four times the maximum break-even figure for commercial application. Consequently, this approach was dropped until such a time that a less costly encapsulating procedure, particularly for particles in the 8-2000 micron range, was devised or until a method was discovered to provide encapsulation of water-soluble salts.

Phase change materials (PCMs) for thermal energy storage applications offer advantages over materials such as water or rocks, whose thermal storage capacity is based exclusively on sensible heat. These advantages include higher energy density, less temperature variation, and, as a consequence, higher heat collection efficiency. Nevertheless, the PCMs have their drawbacks. Compared with water or rocks they are generally higher in cost, lower in heat transfer rates, and more corrosive. In addition, many PCMs can undergo phase separation. Widespread application of PCMs in heat storage systems will depend on cost effective packaging materials and configurations for the PCMs, and appropriate heat exchange systems.

Although each of the earlier-discussed approaches to energy storage offers a partial answer to heat storage problems, a versatile solution that combines flexibility in material selection, full utilization of latent heat, high production efficiency, and long term reliability of the heat storage system remains to be invented. The product of this invention and the process for preparing the product provided such a

solution.

Another serious problem must be overcome when phase-change materials are placed within rigid materials of construction, such as concrete, is the problem of expansion of the PCMs upon phase-changes, resulting in fractures and serious damage to the construction material. The product and process of this invention overcomes this otherwise serious problem.

- 10 This invention provides a process for solid state encapsulation of both water soluble and insoluble PCMs employing common, commercially available raw materials and well-known equipment. One aspect of the process involves pressing PCMs into aspirin-size tablets which are then coated with organic resin formulations. The size of the resulting capsules lies between that of plastics spheres and microcapsules. The capsules are small enough to provide efficient heat transfer and to prevent possible phase separation, yet are large enough for low-cost mass production. Because the capsules are designed to be used in large quantity for long term thermal cycling applications, the durability, flexibility, and cost of the capsule wall materials are

- 25 important parameters.
The product of this invention is a thermal energy storage capsule, capable of incorporation within rigid building construction components without causing fracture or damage to the components or product after the product undergoes repeated thermal change cycles. In detail the capsule comprises a thermal energy storage material capable of undergoing a reversible phase change from solid to liquid, or to an intermediate transitional state comprising both solid and liquid phases, over a given temperature range encapsulated in an encapsulating wall member of a material that is inert with respect to the thermal energy storage material and stable over said temperature range, the wall member comprising at least one seamless structural layer completely surrounding said thermal energy storage material and defining in the capsule a cavity accommodating said thermal energy storage material, said cavity having a volume such that at no time does the volume of the thermal energy storage material, whether in the solid, liquid or transitional state exceed the volume of the cavity, and wherein the total volume of the material forming the wall of the capsule is from 5 to 30% of the total volume of said cavity.

- 50 It is preferred that the outer shell of the capsule has convex shaped outer surfaces with rounded edges and that it should comprise a plurality of seamless coatings of the wall-forming material. Desirably the interior surfaces of the capsule be coated with a primer substance that is water resistant and non-reactive with both the phase-change composition and the wall-forming material, such as asphalt or an acrylic polymer, and that the primer substance volume be less than about 5% of the volume of the cavity.

- Preferred wall-forming materials are selected from the groups consisting of copolymer latex of butadiene-acrylonitrile, copolymer of vinylidene chloride-acrylic, resinous latexes, rubber latexes, epoxy polymers, polyurethane polymers, acrylic polymers,

cellulose acetate and polyamides.

- Preferred phase-change materials are a glauher salt eutectic mixture, sodium hydroxide, polyethylene, sodium sulfate decayhydrate, sodium thiosulfate pentahydrate, calcium chloride hexahydrate, magnesium nitrate hexahydrate, the eutectic of magnesium nitrate hexahydrate and ammonium nitrate, potassium fluoride tetrahydrate, sodium acetate tri-hydrate, stearic acid, the eutectic of naphthalene and benzoic acid and paraffinic hydrocarbons.

- It is preferred that the liquid density of the phase-change material is at least 85% but less than 100% of its solid density when formed as a compacted powder.

- The thermal energy storage capsule of this invention can be incorporated within and be dispersed throughout rigid construction building components such as various concretes (conventional concretes, polymer, epoxy, or polyester) or gypsum, preferably in an amount that is less than about 75% of the total weight of the final components, preferable 20% to 50% by weight. Such components can be all or a part of a building's walls, floors or ceilings.

- It is essential that the volume of the phase-change material within the cavity not exceed the volume of the cavity at any time, regardless of whether the material is in its liquid or solid state or in a transition state, comprising both solid and liquid phases. If the cavity volume is exceeded, the product might be damaged upon thermal cycling, but the most serious problem is that if such a product is incorporated within rigid construction components, such as conventional concretes, the construction component will fracture or suffer other damage after undergoing thermal cycles due to the product expansion.

- In a second aspect this invention provides a process for making thermal energy storage capsules, which comprises forming discrete quantities of a thermal energy storage material into coherent structural bodies having an apparent density that is equal to or less than the liquid phase density of said material, said material being capable of undergoing a reversible phase change from solid to liquid, or to an intermediate transitional state comprising both solid and liquid, over a given temperature range, depositing onto said coherent bodies so as to form a continuous coating surrounding each of said bodies, one or more layers of a self-supporting, capsule-wall-forming material, the or at least one of said layers providing a continuous seamless layer completely surrounding each respective body of thermal energy storage material, heating the encapsulated product to above the melting point of the thermal energy storage material thereby to melt said bodies and form a continuous body of liquid thermal energy storage material encapsulated within a self-supporting capsule wall member formed from said coating of capsule-wall-forming material, and cooling the heated product to solidify the thermal energy storage material inside the capsule.

- In this method it is essential that the apparent solid density of the bodies to be encapsulated does not exceed the liquid density of the thermal energy storage material in question. The apparent solid

density is the weight of the coherent body of phase change material divided by its total volume -- measured as if the outer surfaces of the body were completely impermeable and sealed. In practical effect, the coherent body of phase change material provides a casting mold about which the shell member of the capsule is cast and defines the size of the cavity within the capsule. Thus, upon melting, the volume of the melted composition cannot exceed the volume of the cavity and moreover cannot do so ever again.

In the process of this invention the undercoated coherent bodies of phase change material can be prepared for example by agglomeration from the melted phase-change composition, or by compacting and pelletizing a flowable powder of said phase change material.

Most inert wall-forming materials can be used in the coating steps including polymer latexes, ceramic mixtures, and solvent-based polymer systems. The wall-forming compositions used in the other techniques disclosed above have been severely limited in selection and only gelatin, nylon and urea types were practical candidates. In some cases, polymer walls can be formed during the roll coating procedure by spraying monomer mixtures into the coating machine. Crosslinking reactions can also be carried out either during encapsulation or as a post-treatment step. The wall material serves to hold the shape of the thermal energy storage material, prevent agglomeration, prevent migration or components of the thermal energy storage material, and provide surface area for contact with heat transfer media. It also prevents leaching of the thermal energy storage material. For specific heat and heat of fusion type thermal energy storage compositions, the wall is designed to prevent penetration of the heat transfer fluid.

In a preferred variation, the capsule walls are made inert so that the capsules can be potted in building materials such as plastics or concrete to provide passive storage without seepage or chemical interaction with the substrate.

An important feature of the process and product is that the composition be coated with at least one and preferably two seamless layers of inert wall-forming material in an amount ranging from about 5% to about 30% by weight of the product. Additional layers which may be seamed or seamless may be present as desired.

Among the features and advantages of this invention is the provision of a method of packaging thermal energy storage materials so that they can be used cost-effectively in direct contact heat exchange systems and as additives to plastics, concrete, and other building materials. Another feature is the provision of a protective cover around the typical pill-to-marble-sized, i.e. having a maximum dimension in the range 1/8 to 1 inch (3.2 to 25.4 mm), quantities of thermal energy storage materials to protect them from heat transfer fluid or other agents. Other features are the prevention of leaching and separation of thermal energy storage components, as well as agglomeration of the thermal energy storage material. Other features include a large

surface area for heat transfer to occur; providing a method of attaining energy dense, cost-effective thermal energy storage systems. This invention reduces system costs while providing a way to save energy by permitting convenient use of periodic energy supplies.

This invention will be further described with reference to the accompanying drawings in which:

Figure 1 illustrates the method of this invention by which the thermal energy storage material is encapsulated; and

Figure 2 shows an enlarged storage capsule of this invention.

In the method of this invention as shown in *Figure 1* the thermal energy storage material *3* is placed in a chamber *1* for coating with various materials to form the product of this invention.

Examples of suitable thermal energy storage materials for use in this invention are sodium sulfate decahydrate, sodium thiosulfate pentahydrate, calcium chloride hexahydrate, magnesium nitrate hexahydrate, the eutectic of magnesium nitrate hexahydrate and ammonium nitrate, potassium fluoride tetrahydrate, sodium acetate trihydrate, stearic acid, the eutectic of naphthalene and benzoic acid, and paraffinic hydrocarbons. Preferred are: sodium sulfate decahydrate, sodium thiosulfate pentahydrate, calcium chloride hexahydrate, magnesium nitrate hexahydrate, stearic acid and paraffinic hydrocarbons.

In all cases the thermal energy storage material can be used by itself or with additives that may impart stability or enhance performance in a number of ways. For example, the additives may impart effects on the cooling/heating curve profile, such as reduction of supercooling, they may be used to change the melting point to meet various applications, or they may be helpful to bind component powders so that pellets can be formed without crumbling or to help provide the correct relationship between the apparent solid density and the liquid density of the composition. These additives are known in the art. In all cases, the choice of thermal energy storage material will depend upon the temperature at which the capsule is to operate.

When the thermal energy storage composition is selected, it is pressed into pellets under conditions of temperature, pressure, and time that are governed by the individual thermal energy storage material. The size and shape of the pellets are dependent on system engineering specifications. The pellets can be small or large but a preferred size is between that of a typical pill and a marble, that is, having a maximum dimension in the range 1/8 to 1 inch (3.2 to 25.4 mm). The shape can be simple or intricate, but a preferred shape is shown in *Figure 2*. Conventional commercial pelletizing machines can be used, similar to those now used to make pharmaceutical pills, nuclear fuel pellets, and the like.

With reference to the *Figures*, once the thermal energy storage material has been compressed or compacted into pellets *3*, they are placed in chamber *1*. Chamber *1* is a rotating drum having exhaust ports *2* and attached to motor *4*, which is supported by base *14*. Motor *4* is adapted to rotate chamber *1* to

cause movement of the pellets 3. At the same time, air blower 7, which may employ air heater 8, directs a flow of air 9 into contact with pellets 3. Exhaust air 10 escapes through the mouth of chamber 1 and through ports 2. Spray pump 5 is adapted to deliver various materials 6 for coating on the pellets 3. As is apparent from Figure 1, rotation of chamber 1 by motor 4 and use of air blower 7 and/or spray pump 5 permits the application and treatment of a variety of material on the pellets 3.

The properties of the encapsulating layer depend on the choice and characteristics of the sprayed material, the thickness of deposit, and the mechanism of fixing. For specific heat and heat-of-fusion thermal energy storage materials, walls are desired that are impervious to heat transfer fluid and the thermal energy storage material itself. Thick, strong walls that may be crosslinked or post-cured are required. Examples of wall materials are resinous latexes such as Goodrich Geon 576, 652, 2679, 2600X4, 660X1, and 660X2 and Rohm & Haas Rhoplex AC1230, MU17, MU2, and MU9. Other examples include rubber latexes and epoxy, polyurethane, and acrylic polymers. A balance among cost, performance and the intended use contribute to the selection criteria. In some instances more than one material may be desirable. For example, a first encapsulating layer may be deposited that has a high degree of elasticity, allowing it to absorb the stresses of thermal energy storage material expansion and contractions. A second, outer layer may then be deposited that has less elasticity but is more impervious. Many variations in the processing are possible and, in fact, are determined by the nature of the thermal energy storage composition and the requirements of the particular application. For example, pellets having strong tendencies to flake, chip or crumble may require a thick coating with a low molecular weight polymer prior to vigorous tumbling in the roll coater.

In a preferred embodiment, the thermal energy storage capsule of Figure 2 is manufactured, using the device shown in Figure 1. Pellets 3 are loaded into chamber 1. Blower 7 is started as is motor 4 to rotate the pellets 3 in the presence of forced air 9, which removes fines and dust from the tablets. Heater 8 is energized to dry the pellets if necessary, which at this time consists of one of the thermal energy storage compositions 17 shown in Figure 2, while maintaining the temperature below the melting point of the phase-change composition. A primer 18 is coated onto the composition 17 via spray pump 5. This primer 18 serves to seal the core material 17 from other coating materials. Quite often, most of the salts used for latent heat storage-type compositions will cause coagulation of latex-type coating materials. The primer should be a material which is chemically inert with respect to both core material and the coating. A preferred primer material is an asphalt material which has been thinned with a hydrocarbon solvent. Such a primer also improves the adhesion of the coating to the core. Another function of the primer is to indicate the degree of damage to the capsule during the remainder of the process. Since the primer is often

times a different color than the core, such as with asphalt, damage or imperfections to the core are revealed by a change in color. While one primer coat may be satisfactory for some applications, it is sometimes necessary or desirable to apply several primer coats, up to approximately 2% by weight, based on the core material 17. Drying, such as by air or heated air circulated by blower 8, is preferred. However, for good adhesion, the asphalt or other primer must be allowed to soak into the surface of the tablet. If the drying step proceeds too rapidly, the primer may quickly wear off during the subsequent processing. On the other hand, if drying is too slow, the tablets may stick together in large clumps between primer applications.

After the final coat of primer 18, while it is still wet, a layer of mica 19 or other similar material is applied in an amount sufficient to increase the weight of the product by approximately 0.5%. The mica layer 19 serves as a water vapor barrier and helps to prevent tablet agglomeration.

Next, a thin layer of a quick-drying resin with good adhesion and covering characteristics, as well as good elasticity, is applied. This resin 20 may be a latex, such as butadiene-acrylonitrile copolymer latex or other similar resin added through spray pump 5. Satisfactory products can be prepared by using such a polymer in the amount of approximately 3% by weight of the product. This layer 20 may be deposited all at once or by the application of a multiplicity of very thin layers. It is essential that the covering or coating be seamless, so that subsequent use of the product will not have a joint or junction which can be subjected to successive stress. The advantage of this highly-resilient resin is that it protects the relatively brittle primer layer 18, which would otherwise be damaged by friction between tablets as they are tumbled in the coating drum. The acrylonitrile layer cushions the tablet during the remainder of the process and also adds additional desirable elasticity to the finished wall.

The major portion of the structural wall 21 is next applied which provides structural strength and resistance to moisture vapor transmission. If this wall material has too high of a permeability factor, the phase change material, thermal energy storage composition, will lose its hydration, causing the loss and possible damage to the product's environment of heat-storage capacity. One preferred polymer for this part of the wall is the copolymer of vinylidene chloride-acrylic copolymer. This final wall component will preferably comprise approximately 15% of the weight of the finished product. It is necessary that the wall be built from very thin coats and be properly cured between applications to prevent the formation of seams. Proper curing is indicated by a combination of three factors: surface tackiness, transparency and shininess. Thick coats, resulting from excessive coating application or improper curing, might cause the tablets to stick together and pull as they are tumbled, causing bumps and thin spots in the walls. These imperfections may cause the tablet to fall early in use. If the coating is being properly applied, the resulting wall will be smooth, shiny and transparent. Periodically, the curing air

should be gently heated to speed up the curing process. Nevertheless, the temperature should be maintained at all times during manufacture below that at which the core material 17 will melt. As the wall 21 is nearing completion, a dusting of mica 22 or similar material can preferably be added between the latex layers. This addition will again improve vapor transmission resistance. The final outer layer 23, preferably of the same composition as layer 21, and the previous outer layer 21 combine to comprise approximately 20% of the finished product weight. Thinner walls are, of course, possible and thicker walls can be employed if desired. Normally, the total amount of wall forming material comprising the shell member will range from about 5% to about 30% by weight of the total product.

The invention is further illustrated by the following examples.

20 Example 1

A glauber salt eutectic mixture, having a melting point of 73°F, (23°C) was formulated as follows: sodium sulphate, 17%; sodium carbonate, 20%; borax, 3%; clay, 3%; water 57%. This mixture was chilled and passed through a tableting machine as a flowable powder and formed into pellets. The tableted pellets are then encapsulated in asphalt, which has been thinned with hydrocarbon solvent as primer layer 18, followed by the addition of mica layer 19. The two latex materials described above were used to form layers 20, 21 and 23. Layer 20 was formed from butadiene-acrylonitrile latex and layers 21 and 23 from vinylidene chloride-acrylic copolymer. Mica was again used for layer 22. The various layers which were applied to form the coatings were seamless. These layers were built up as the product rotated in the drum, and were substantially uniform in thickness. The amounts of the various coatings, and the volumetric relationships, were at about the midportions of the ranges specified in the Brief Summary of the Invention.

The pellets are convex tablets with rounded edges measuring about 1/2 inch (13mm) in diameter and about 3/8 inch (9.5 mm) thickness after final coating.

During the tableting step, the compaction was controlled to provide an apparent solid density of 1.10, the liquid being 1.28, g/cc..

Each of the two products is performance tested by dispersing 30% by weight of the product throughout a standard size conventional concrete mortar mix brick, and the brick and product then allowed to cure 3 days. The brick is then heated to 160°F (71°C) and held at this temperature for several hours. The brick is then subjected to numerous changes in temperature, cycling above and below the phase-change melting point. No fractures or other damage to the brick or products are observed.

Example 2

In this example, a sodium sulphate decahydrate thermal energy storage material comprising 42% sodium sulphate, 3% borax, 3% clay and 52% water is formed into a product according to the present invention. The ingredients are passed several times through a colloid mill to reduce the particles to

micron size and thereby fully hydrate the salt and form a completely homogeneous suspension of all the components. When milling is complete, the phase change material mixture is solidified and ground to pass through a number 8 sieve. This degree of fineness is desirable for proper flow characteristics during pelletization. Solid lubricants, such as lithium stearate, may be added in trace amounts to improve the flow and compression characteristics during the pelletization.

This bulk material is conveyed to a tablet-forming press of standard design. The powder flow is from a feed-hopper to the compression chamber where a charge is sized and shaped according the press dies in the machine. The standard shape of the tablet is that of a short cylinder with convex ends. Tablet diameter is about 1/2 inch (13mm) with a thickness of about 3/8 inch (9.5 mm). The compression is controlled so that the tablet has an apparent solid density which is equal to the liquid density (1.47) of the composition. The solid density of the phase change composition is 1.56 g/cc.

The various encapsulation steps described in Example 1 are then carried out such that the finished product will have a cross-section as shown in Figure 2 of the drawings. When performance tested as in Example 1, no fractures or failures of the brick are observed.

95 Example 3

The procedures of Examples 1 and 2 are repeated for each of the following phase change compositions: glauber salt eutectic mixture, sodium hydroxide, polyethylene, sodium sulfate decahydrate, sodium thiosulfate pentahydrate, calcium chloride hexahydrate, magnesium nitrate hexahydrate, the eutectic of magnesium nitrate hexahydrate and ammonium nitrate, potassium fluoride tetrahydrate, sodium acetate trihydrate, stearic acid, the eutectic of naphthalene and benzoic acid and paraffinic hydrocarbons.

Each of the pelletized compositions is then encapsulated just as in Example 1.

Each of the above phase change compositions is then encapsulated as in Example 1 with the following separate materials for layers 20, 21 and 23 (same material for each layer): a copolymer latex of butadiene-acrylonitrile, a copolymer of vinylidene chloride-acrylic, resinous latexes, rubber latexes, epoxy polymers, polyurethane polymers, acrylic polymers, cellulose acetate and polyamides.

These encapsulated products are performance tested as in Example 1 and no fractures or damage to the bricks or products are observed.

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Example 4

The structures for encapsulation earlier described can be formed by means other than by compaction of powdered PCM chemicals, as illustrated in this example. Another method is that of agglomeration, either in rotating pans, fluidized bed machines, or devices having characteristics of both these types. In a rotating pan agglomerator, seed crystals are sprayed with molten material while the pan turns. Density of the particles can be controlled by varying

the temperature and droplet size of the sprayed molten, phase-change composition, and by rotation speed and cooling of the pan. Structure size is controlled by duration of the cycle and size of the seed crystals. The structure formed will be either spherical or egg-shaped.

A fluidized bed agglomerator can form structures for subsequent encapsulation by similar spraying of molten material on seed crystals, but in this case, the pellets are suspended in an air stream, and behalf, in bulk, as fluid (i.e. having a zero angle of repose). Some particle formation is caused by collision and adhesion of relatively large particles. As a general rule, particles agglomerated in a fluid bed are more irregular in shape and of lower density than the product of rotating pan agglomerators. Degree of fluidization is a factor in the final density of the formed particle, as is the characteristics of the spraying into the fluidized bed.

Optimum control of the particle size distribution, shape, and density can be achieved with a device that combines characteristics of both the above machines (Glatt Air Techniques is one manufacturer of such a device). The particles are formed in a rotating pan that has a slot at the outer circumference of the pan bottom. Through this slot, air sufficient to somewhat fluidize the particle bed is admitted. The major factors that govern particle density in this rotary-fluidized bed granulator are: pan rotation speed, fluidizing air temperature, and PCM application rate. The size of the air admitting slot has a minor effect. Through proper combination of the control factors, the density of the PCM particle formed can be controlled to that necessary for the proper performance of the finished product. The rotary-fluidized bed granulator just described can also be configured to properly apply the various coating materials previously described, giving the potential of complete fabrication of the PCM capsule with one machine.

Pellets of sodium sulphate hexahydrate (Glauber's salt) are formed in a rotating pan type granulator as described above. The PCM is applied at a temperature just above melting temperature in a fine spray to form egg-shaped particles ranging in size from $\frac{1}{2}$ to $\frac{3}{4}$ of an inch (13 to 19 mm) in diameter. The density of the PCM pellets is found to be slightly less than the 1.47 g/cc of the molten PCM as deemed essential in this invention. The particles are then encapsulated as described in Example 1. After performance testing as in Example 1, no damage to the product or the construction materials is observed.

Examples 5 and 6 again demonstrate the criticality of the density relationship of the phase-change structures and the densities of the phase-change composition *per se*, in each of its states.

Example 5

A similar product using calcium chloride hexahydrate was prepared. This material is highly hygroscopic, and for that reason precautions must be taken during pelletization and encapsulation to prevent the adsorption of water from air to the surface of the tablets. This surface water would prevent coating

film formation or possibly even dissolve the tablet.

Calcium chloride hexahydrate is commercially available with various stabilizing additives premixed therein. The tablet-forming is accomplished under conditions whereby the equilibrium humidity, namely about 35% is maintained to prevent adsorption of water from the air.

During the encapsulation step, the primer coat of asphalt must be thicker to ensure chemical isolation of the salt from later-used latex materials due to the fact that the salt coagulates most latexes. Therefore 5% asphalt, based upon the total weight of the product, is applied. Mica is also added, and the remaining layers are then applied, as previously described in Example 1.

The apparent solid density of the structure before coating is about 1.55 g/cc and the liquid density of the phase-change composition is 1.35 g/cc. Thus, when the phase-change composition melts, its volume will exceed the volume of the cavity of the product. The product size is about 5/16 inch (8mm) in diameter and $\frac{1}{4}$ inch (6 mm) in height.

When performance tested as in Example 1, the construction materials shatter upon initial heatup, as the density relationships above-mentioned are outside of the critical requirements for the product of this invention.

Example 6

A similar product was prepared, without difficulty using the process of this invention, except as otherwise pointed out, in which a commercially available paraffin, having a melting point of 116°F (47°C), was used. A 5% addition of stearate was necessary to improve powder flow and compaction properties. The tablets were formed as previously described. Encapsulation of this material is far easier than those previously described. The primer coating of vinylidene-chloride-acrylic copolymer readily adheres to the wax and forms a strong, tight coating. The application of a butadiene-acrylonitrile latex followed by an additional vinylidene chloride-acrylic copolymer results in a finished product as shown in Figure 2.

The apparent solid density of the compacted structure before coating is 0.87 g/cc and the liquid density of the composition is 0.80 g/cc. As expected, the product failed in the performance test, as in Example 5 above, as the volume of the cavity of the product shell member was less than the liquid volume of the wax composition.

The above products of Examples 1-4, prepared according to the examples described herein, were evaluated as thermal energy storage products. The products were evaluated over a variety of heat-cycle tests. These tests quite successfully showed that all of the properly encapsulated compositions described above were cycling through heat and cold cycles without failure such that a twenty-year commercial life or more is anticipated for all of these products. This is to be contrasted with results of evaluation efforts which were made on compositions in which the apparent solid density exceeded the liquid density of the composition, as in Examples 5 and 6. Inevitably, these highly compacted products

failed during cycling due to expansion during transition from the solid to the liquid phase. Similarly, a number of thermal energy storage products were prepared as in Examples 1-4, except during the encapsulation step, a seam was permitted to form in the layers closest to the thermal storage composition. After some degree of cycling, the capsules failed, with the phase change compositions leaking from the capsules at the seams in the capsule.

CLAIMS

1. A thermal energy storage capsule comprising a thermal energy storage material capable of undergoing a reversible phase change from solid to liquid, or to an intermediate transitional state comprising both solid and liquid phases, over a given temperature range encapsulated in an encapsulating wall member of a material that is inert with respect to the thermal energy storage material and stable over said temperature range, the wall member comprising at least one seamless structural layer completely surrounding said thermal energy storage material and defining in the capsule a cavity accommodating said thermal energy storage material, said cavity having a volume such that at no time does the volume of the thermal energy storage material, whether in the solid, liquid or transitional state exceed the volume of the cavity, and wherein the total volume of the material forming the wall of the capsule is from 5 to 30% of the total volume of said cavity.

2. A capsule according to claim 1, wherein the maximum external dimension of the capsule is in the range 1/8 to 1 inch (3.2 to 25.4 mm).

3. A capsule according to claims 1 or 2, wherein the wall member has a multi-layered seamless structure.

4. A capsule according to claim 3, wherein at least two of said layers are seamless layers completely surrounding the capsule.

5. A capsule according to any one of claims 1 to 4, wherein the capsule has a convex external contour.

6. A capsule according to any one of claims 1 to 5, wherein the wall member of the capsule is constructed from one or more of the following: a natural or synthetic rubber latex, a polymer or copolymer of vinylidene chloride or an acrylic monomer, a resinous latex, an epoxy polymer, a polyurethane, cellulose acetate or a polyamide.

7. A capsule according to claim 6, wherein the wall member is constructed from a butadiene-acrylonitrile copolymer latex.

8. A capsule according to any one of claims 1 to 7, wherein the interior surface of the wall member is coated with a primer.

9. A capsule according to claim 8, wherein the primer is a water-resistant primer.

10. A capsule according to claim 9, wherein the water-resistant primer is asphalt or an acrylic polymer or copolymer.

11. A capsule according to any one of claims 8 to 10, wherein the primer coating is present in a volumetric amount that is less than 5% of the volume of the cavity.

12. A capsule according to claim 3 or 4, wherein the wall member comprises a water impermeable barrier provided by a film of mica deposited between two of the superposed structural layers which make up the wall member.

13. A capsule according to any one of claims 1 to 12 wherein the encapsulated thermal energy storage material has a liquid density that is at least 85% but less than 100% of the solid density of that material.

14. A capsule according to any one of claims 1 to 13 wherein the thermal energy storage material has a phase change transition temperature with the range 7°C to 90°C.

15. A capsule according to any one of claims 1 to 14 wherein the thermal energy storage material is a glauher salt eutetic mixture, sodium hydroxide, polyethylene, sodium sulfate decahydrate, sodium thiosulfate pentahydrate, calcium chloride hexahydrate, magnesium nitrate hexahydrate, a eutectic mixture of magnesium nitrate hexahydrate and ammonium nitrate, potassium fluoride tetrahydrate, sodium acetate trihydrate, stearic acid, a eutectic mixture of naphthalene and benzoic acid or a paraffinic hydrocarbon.

16. A capsule according to claim 1, substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings.

17. A method for the manufacture of a thermal energy storage capsule, which comprises forming discrete quantities of a thermal energy storage material into coherent structural bodies having an apparent density that is equal to or less than the liquid phase density of said material, said material being capable of undergoing a reversible phase change from solid to liquid, or to an intermediate transitional state comprising both solid and liquid, over a given temperature range, depositing onto said coherent bodies so as to form a continuous coating surrounding each of said bodies, one or more layers of a self-supporting capsule-wall-forming material, the or at least one of said layers providing a continuous seamless layer completely surrounding each respective body of thermal energy storage material, heating the encapsulated product to above the melting point of the thermal energy storage material thereby to melt said bodies and form a continuous body of liquid thermal energy storage material encapsulated with a self-supporting capsule wall member formed from said coating of capsule-wall-forming material, and cooling the heated product to solidify the thermal energy storage material inside the capsule.

18. A method according to claim 17, wherein said discrete bodies are formed by pressing and compacting a powdered thermal energy storage material.

19. A method according to claim 17, wherein said discrete bodies are formed by agglomeration and solidification of the thermal energy storage material in molten form.

20. A method according to claims 17, 18 or 19, wherein said discrete bodies have a maximum dimension in the range 1/8 to 1 inch (3.2 to 25.4 mm).

21. A method according to claims 17, 18, 19 or 20, wherein the discrete bodies are coated with said

capsule wall-forming material by tumbling or rolling the discrete bodies whilst spraying thereon a liquid composition comprising the capsule wall-forming materials.

- 5 22. A method according to claim 21, wherein successive quantities of said wall-forming materials are sprayed on to the rolling on tumbling bodies in a discrete series of steps, thereby to provide a capsule wall structure having a multiplicity of layers.
- 10 23. A method according to claim 21 or 22 wherein, prior to the application of the wall-forming materials, the discrete bodies of said thermal energy storage material are coated with a water-resistant primer composition.
- 15 24. A method according to claim 23, wherein the water-resistant primer composition comprises asphalt or an acrylic polymer or copolymer.
- 25 25. A method according to claim 23 or 24, wherein the discrete bodies are primed with up to 5% by weight of the primer based on the weight of said bodies.
- 20 26. A method according to any one of claims 22 to 25, wherein the application of two of said layers, the partially coated bodies are given a coating of mica thereby to provide a water-impermeable barrier layer in the capsule wall.
- 25 27. A method according to any one of claims 17 to 26, wherein the thermal energy storage material has a liquid density that is at least 85 but less than 100% of the solid density of the material.
- 30 28. A method according to any one of claims 17 to 27, wherein the thermal energy storage material has a phase-change transition temperature within the range of 7°C to 90°C.
- 35 29. A method according to any one of claims 17 to 28, wherein the thermal energy storage material is a glauher salt eutectic mixture, sodium hydroxide, polyethylene, sodium sulfate decahydrate, sodium thiosulfate pentahydrate, calcium chloride hexahydrate, magnesium nitrate hexahydrate, a eutectic of magnesium nitrate hexahydrate and ammonium nitrate, potassium fluoride tetrahydrate, sodium acetate trihydrate, stearic acid, a eutectic of naphthalene and benzoic acid, or a paraffinic hydrocarbon.
- 40 30. A method according to claim 18 wherein a binder material is added to the powder prior to pressing and compacting to improve integrity of the compacted bodies.
- 45 31. A method according to claim 18, wherein a filler is added to the powder prior to compacting to provide an apparent solid density after compacting that is less than or equal to the liquid density of the thermal energy storage material.
- 50 32. A method according to any one of claims 21 to 31 wherein the wall-forming material is a natural or synthetic rubber latex, a polymer or copolymer of vinylidene chloride or an acrylic monomer, a resinous latex, an epoxy polymer, a polyurethane, cellulose acetate or a polyamide.
- 55 33. A method according to claim 32, wherein the wall-forming material comprises a butadiene-acrylonitrile copolymer latex.
- 60 34. A method according to any one of claims 17 to 33, wherein the wall-forming material is used in an amount sufficient to provide a capsule in which
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the wall-forming material constitutes 5% to 30% by weight of the final product weight.

35. A method according to claim 17, substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

- 70 36. A rigid structural building element having incorporated therein up to 50% by weight of thermal energy storage capsules as claimed in any one of claims 1 to 16 or made by a method claimed in any one of claims 17 to 35.

37. A building element according to claim 36, comprising a gypsum or concrete matrix having said capsules dispersed therein.

38. A building element according to claim 37, wherein the matrix is a concrete matrix selected from conventional hydraulic concrete, polymer concrete, epoxy concrete or polyester concrete.

39. A building element according to any one of claims 36 to 38 in which the thermal energy storing capsules are present in an amount in the range 20% to 50% by weight.

40. A building element according to any one of claims 36 to 39, which is a floor, ceiling or wall element for a building.

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